^{14}C Enrichment of Surface Deposits on Oldbury Reactor Core Graphite Determined by Secondary Ion Mass Spectrometry and Thermal Oxidation/Liquid Scintillation Techniques

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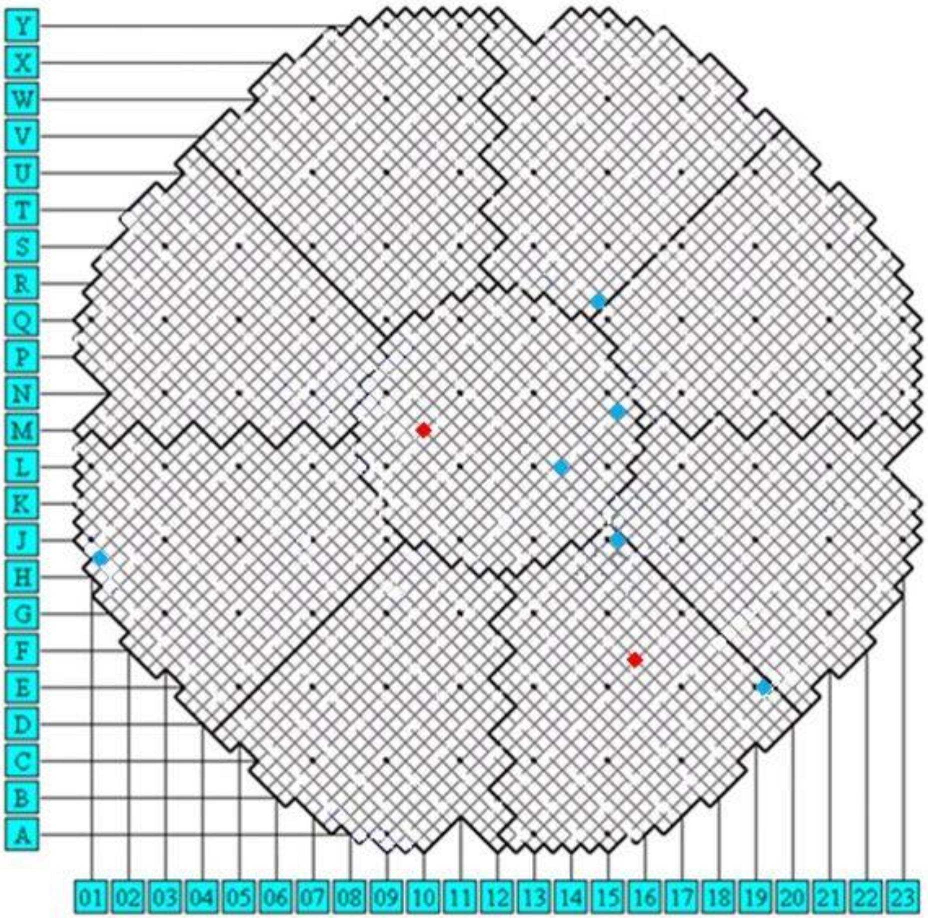
Irradiated graphite

- Historically, the United Kingdom has built a number of graphite moderated reactors.
- Many of these reactors are in the process of decommissioning.
- Majority of the graphite classified as Intermediate Level Waste (ILW).
- Significant quantity for eventual disposal in a Geological Disposal Facility (GDF)

Sample provenance

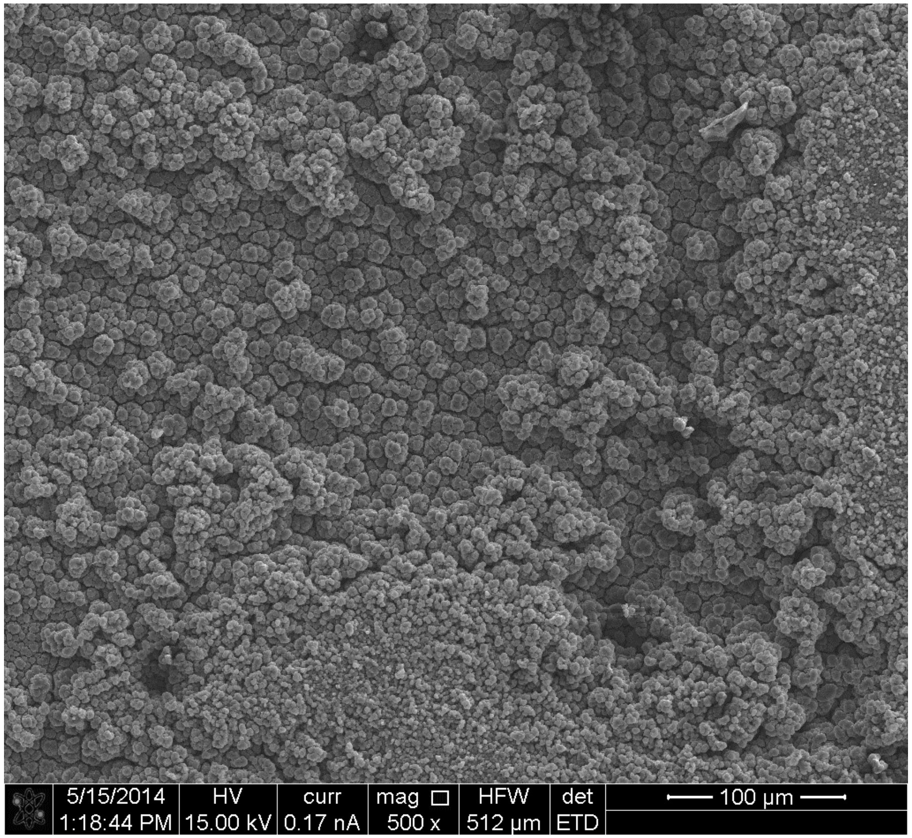


Blue = Fuel Channel

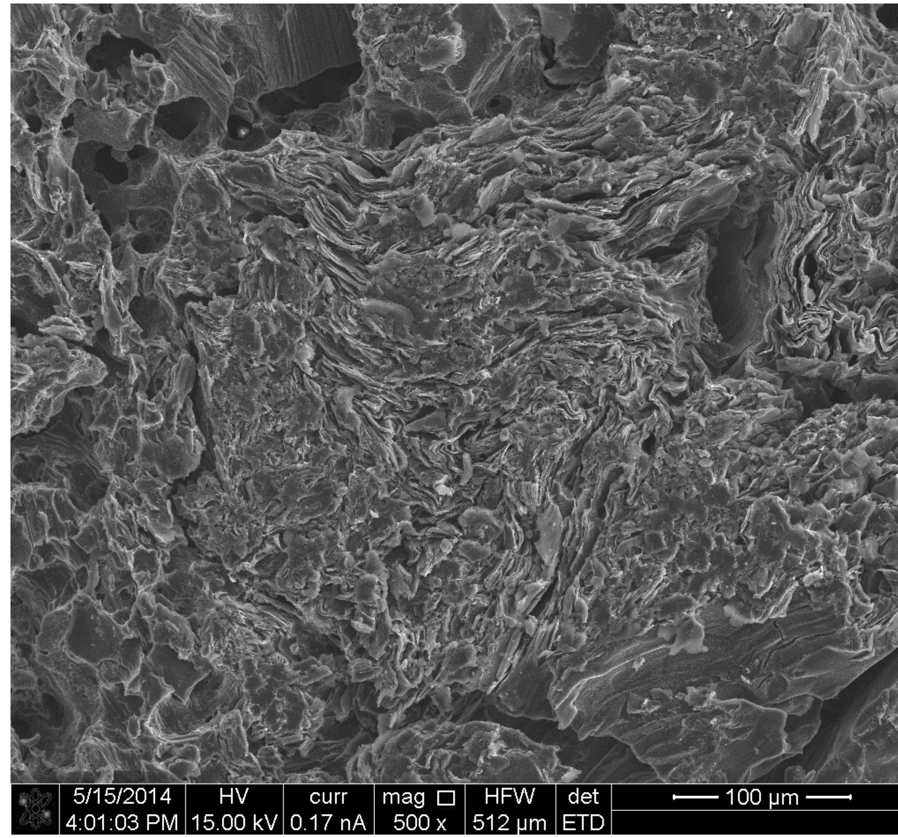
Red = Interstitial Channel

- 49 samples
  - 6 x fuel channels
  - 2 x interstitial channels
- Oldbury reactor one
- Before receiving at UoB:
  - All samples had Bulk Density by Immersion (BDI)
  - One sample (Q15C5 6L/1) analysed for open pore volume and differential thermal oxidation

Scanning Electron Microscopy

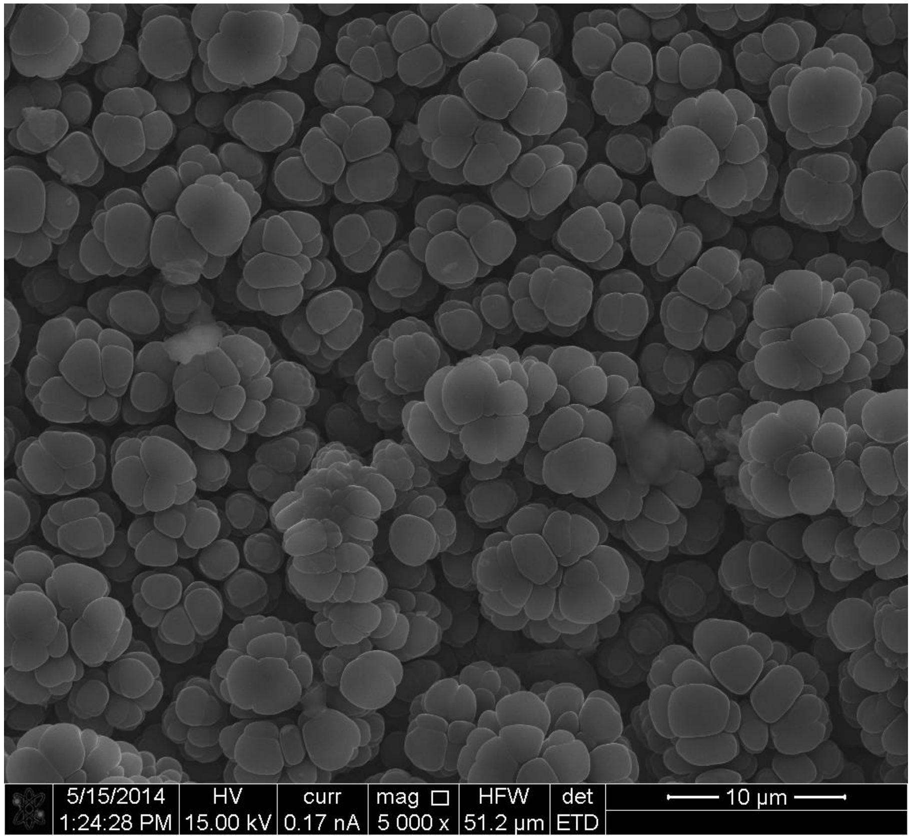


Channel Wall Face

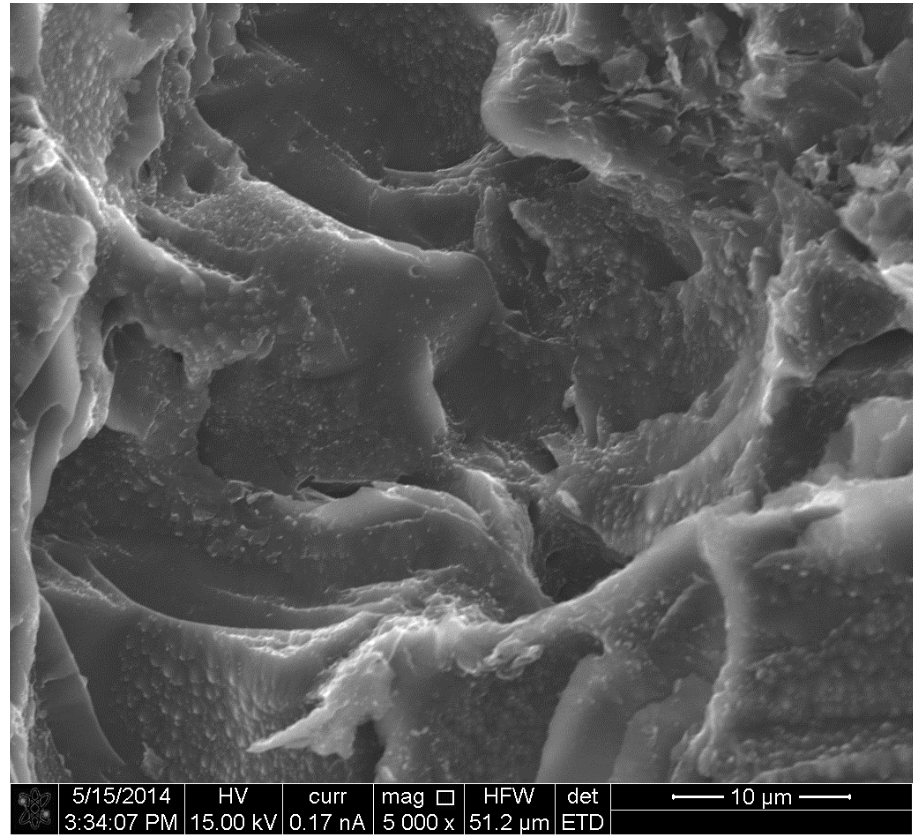


Inner Brick

Scanning Electron Microscopy

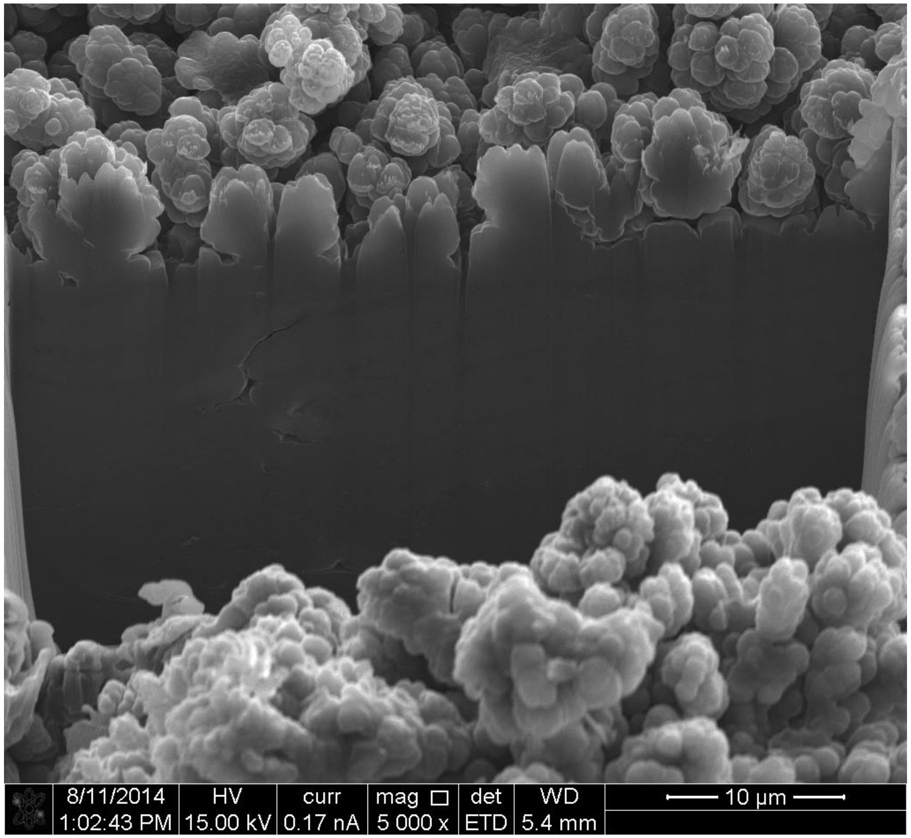


Channel Wall Face

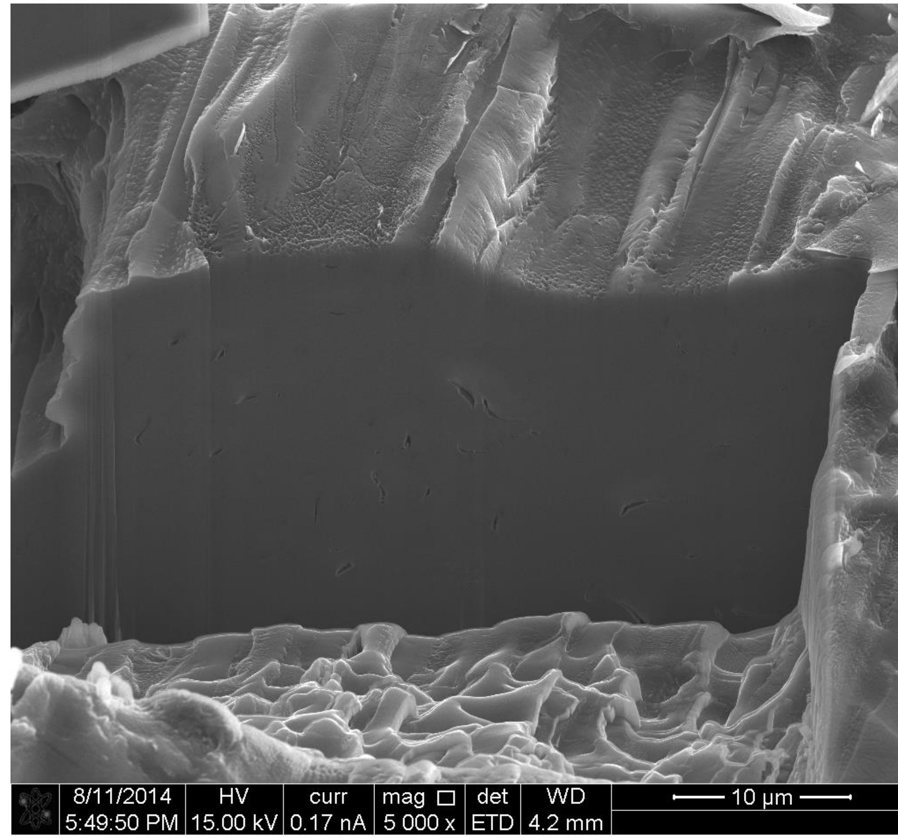


Inner Brick

SEM-FIB

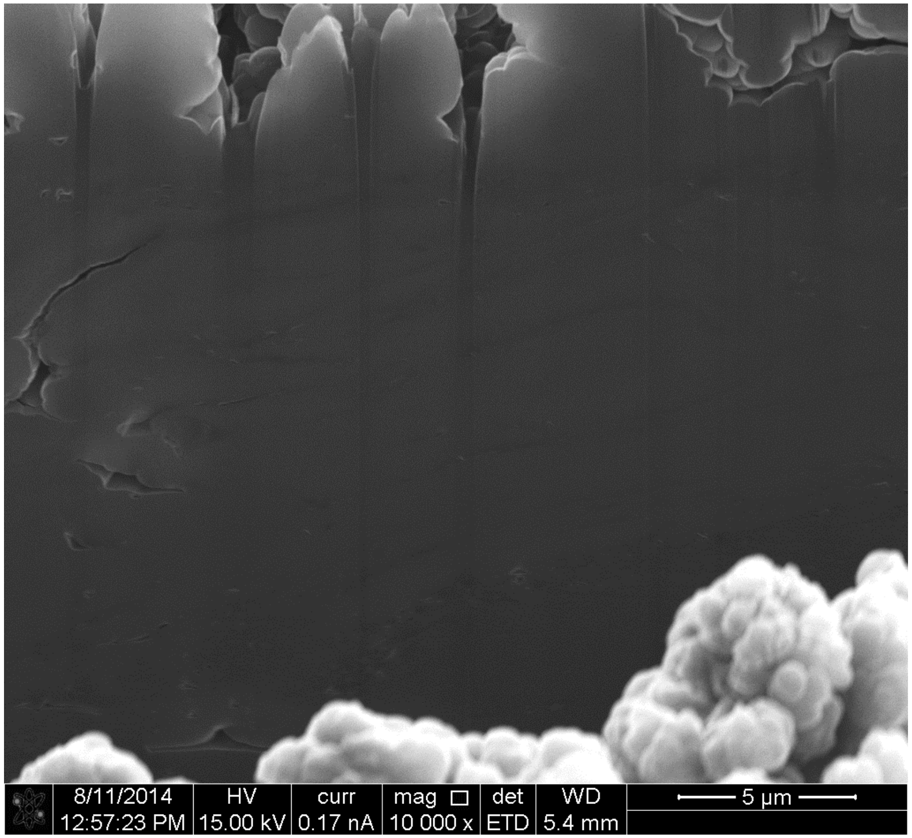


Channel Wall Face

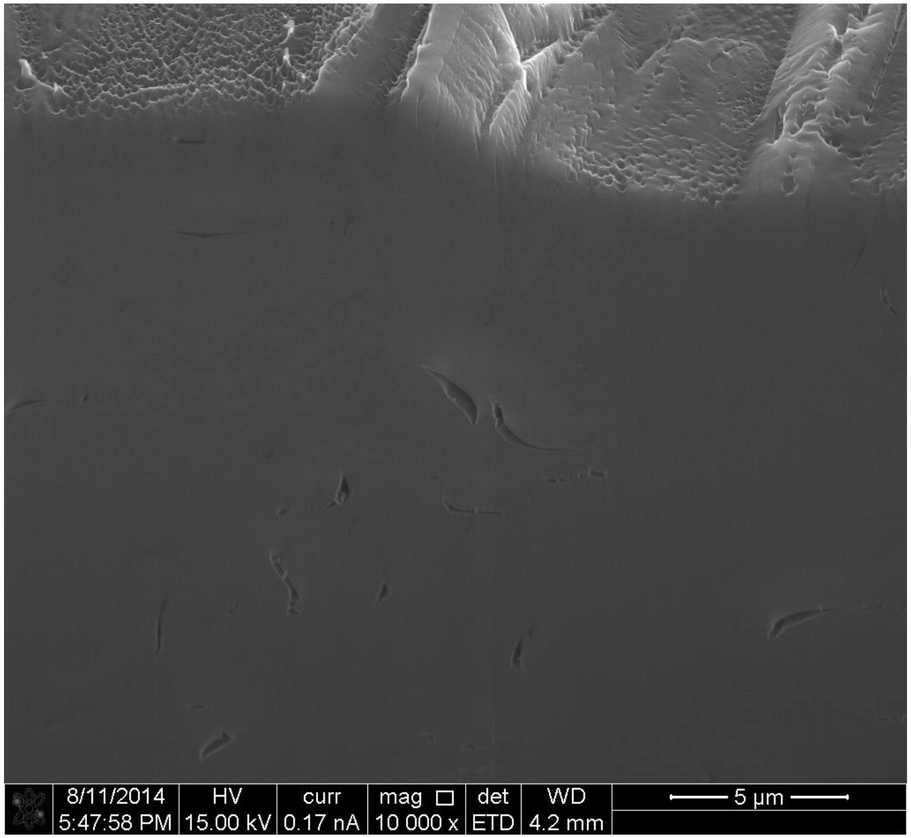


Inner Brick

SEM-FIB

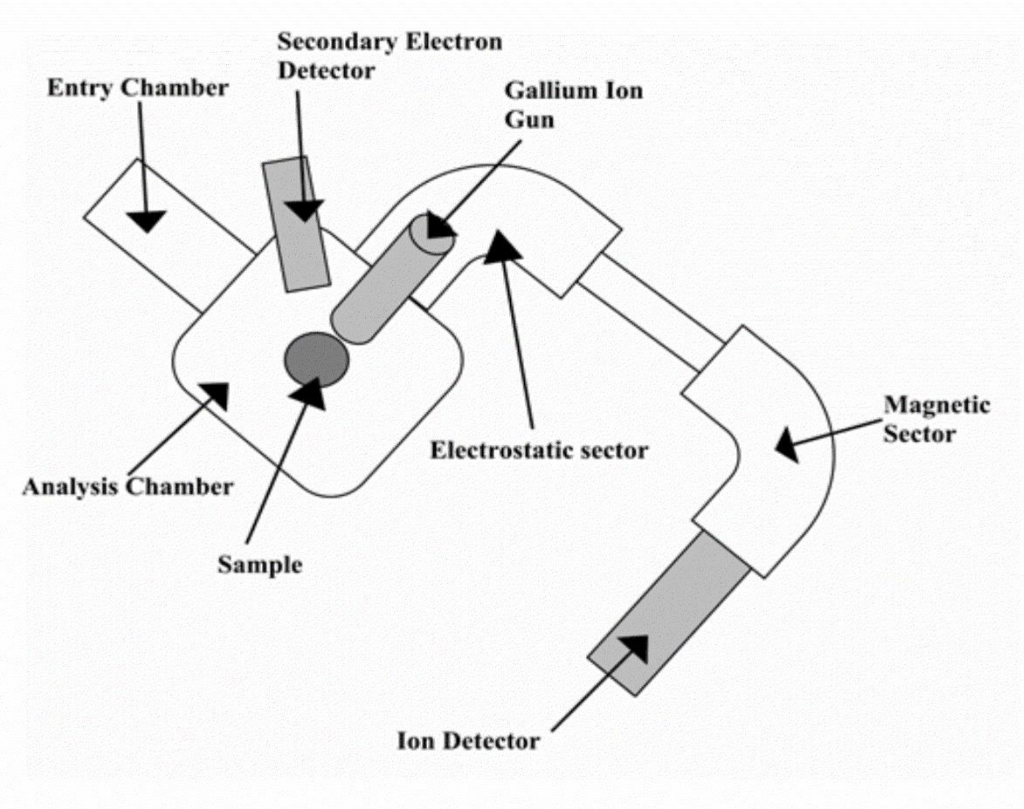


Channel Wall Face



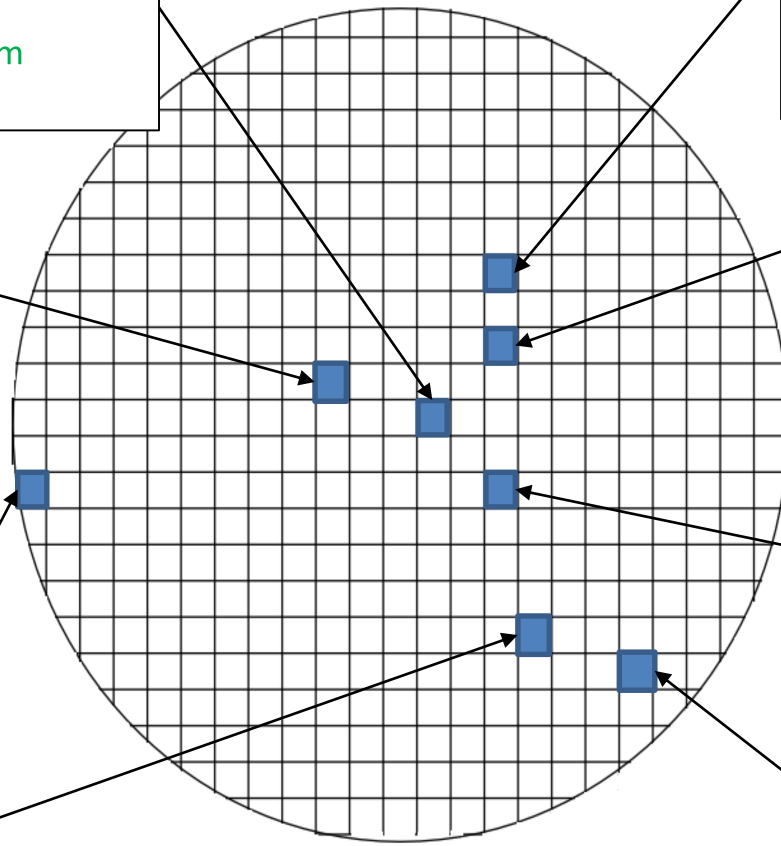
Inner Brick

Secondary Ion Mass Spectrometry



- Incident gallium ion beam sputters the sample surface
- Secondary ion mass fragments generated
- Mass/Charge (m/z) ratio and intensity measured using Magnetic Sector mass spectrometer
- Corrections needed for interference peaks
- Low spectral resolution compared to commercial instruments
- **Ability to analyse radioactive samples**

SIMS Results



L13B2
4L: 28.8 ± 4.3 ppm
EDND: 45.22
7L: 12.8 ± 1.5 ppm
EDND: 49.92

M10
4L: 55.3 ± 6.7 ppm
EDND: 38.18
7L: No coating present(< LOD)
EDND: 42.14

J01A4
4U: No coating present (< LOD)
EDND: 15.42
7U: No coating present (< LOD)
EDND: 15.55

F16
4L: 26.1 ± 3.1 ppm
EDND: 38.18
7L: 22.7 ± 5.5 ppm
EDND: 42.14

Q15C5
2U: 20.8 ± 3.9 ppm
EDND: 26.54
7L: 13.2 ± 3.9 ppm
EDND: 51.22
11U: 5.3 ± 1.8 ppm
EDND: 15.48

N15A4
4U: 24.9 ± 8.9 ppm*
EDND: 28.78
8U: 19.2 ± 1.1 ppm
EDND: 26.49

J15B5
4L: 28.5 ± 4.9 ppm
EDND: 45.52
7L: 6.6 ± 0.6 ppm
EDND: 49.92

E19B5
4U: 24.6 ± 0.8 ppm
EDND: 26.05
7U: 5.4 ± 1.4 ppm
EDND: 23.77

EDND: Equivalent DIDO Nickel Dose
ppm: Parts Per Million

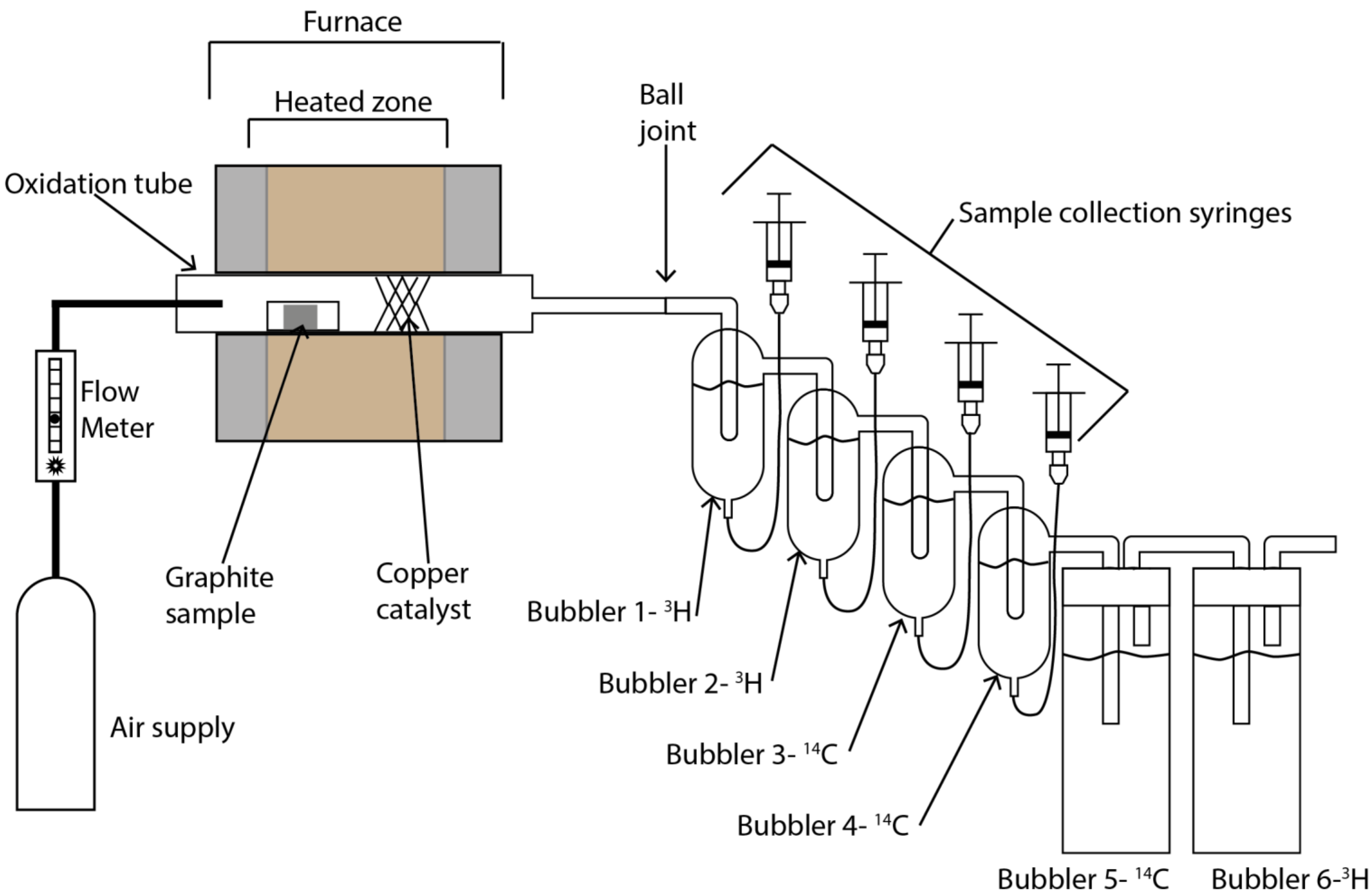
*Indicates thin coating sample

SIMS-Conclusions

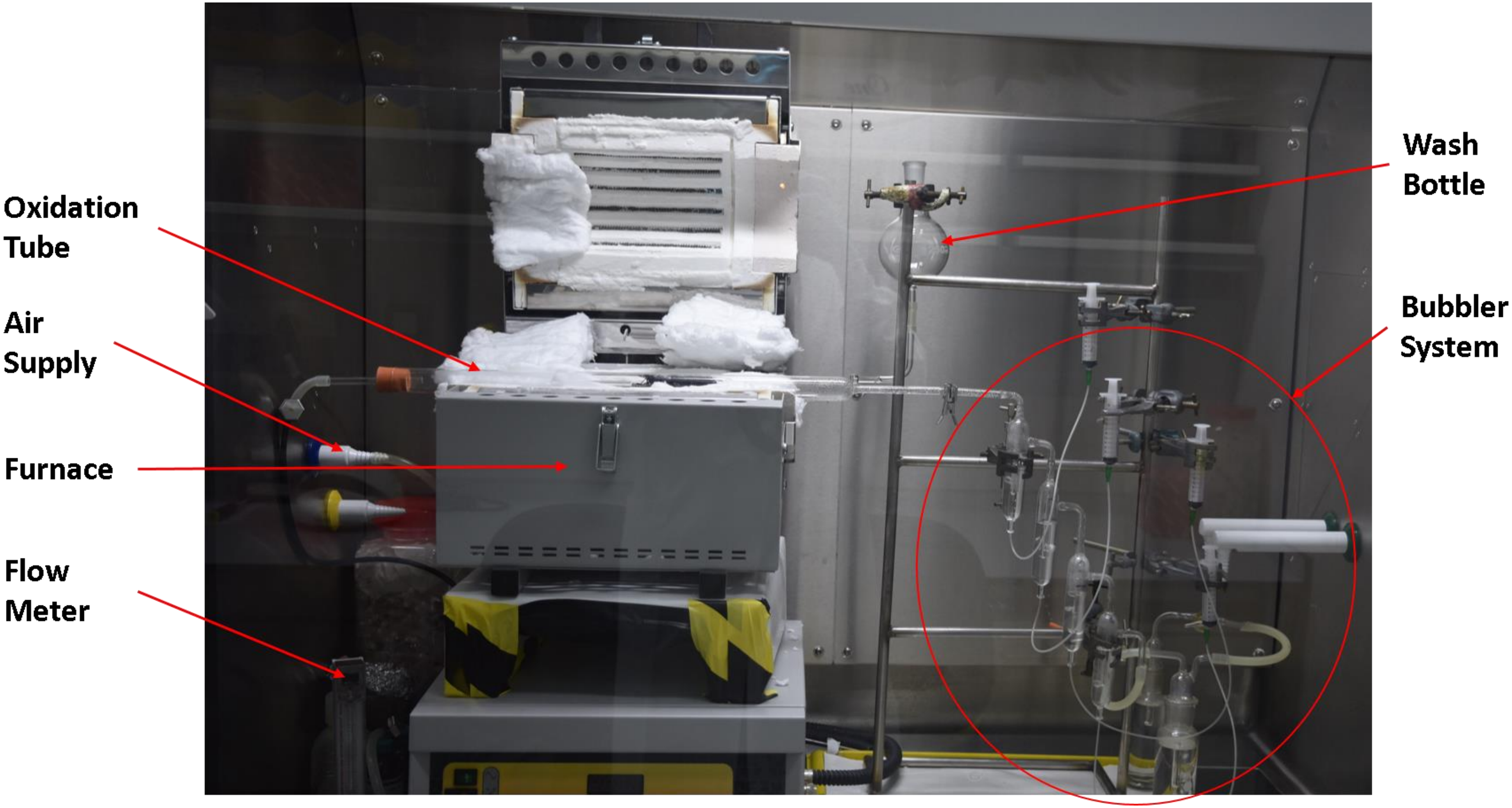
- Inner brick slices give results below the limits of detection (estimated at approximately 2 ppm)
- Channel wall faces appear to be ^{14}C enriched when deposit is present
  - 5-60 ppm
  - Samples lower in the channel appear to have higher concentration
  - Does not appear to be correlated with lifetime neutron dose (EDND)
- Ion maps show the ^{14}C is uniformly distributed in the deposit

For full details see: *L. Payne, P. J. Heard and T. B. Scott. “Enrichment of C-14 on surface deposits of Oldbury reactor graphite investigated with the use of Magnetic Sector Secondary Ion Mass Spectrometry (MS-SIMS).” WMSymposia2015* proceedings

Thermal Oxidation/LSC



Thermal Oxidation/LSC



Thermal Oxidation/LSC

Experimental run 1:

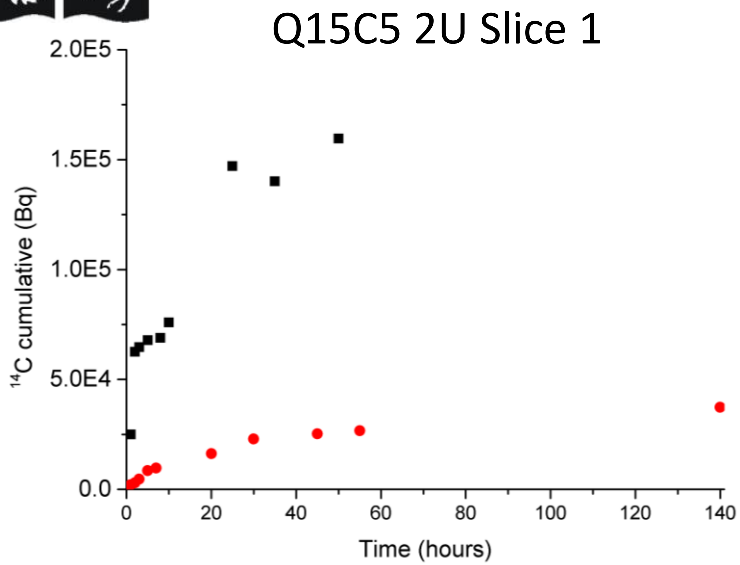
- 450 °C for 50 hours
- 50 mL/min air
- Copper catalyst
- Aliquots taken at 0, 1, 2, 3, 5, 8, 10, 25, 35 and 50 hours
- Counted using LSC for 60 minutes

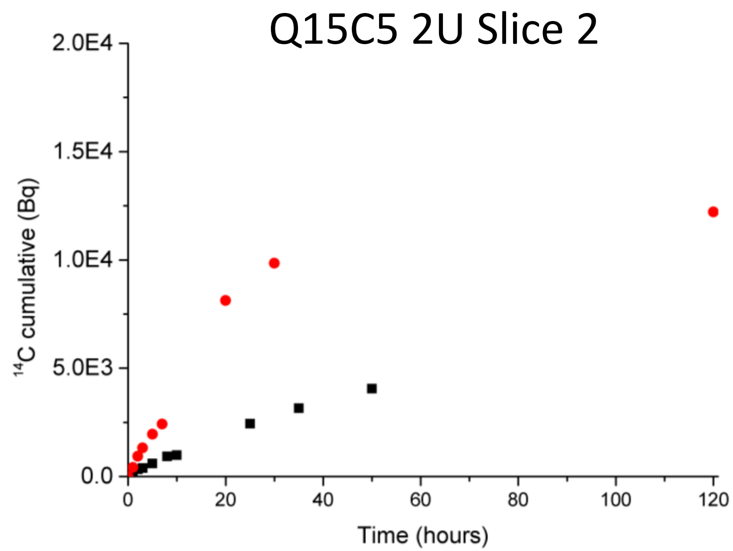
Experimental run 2:

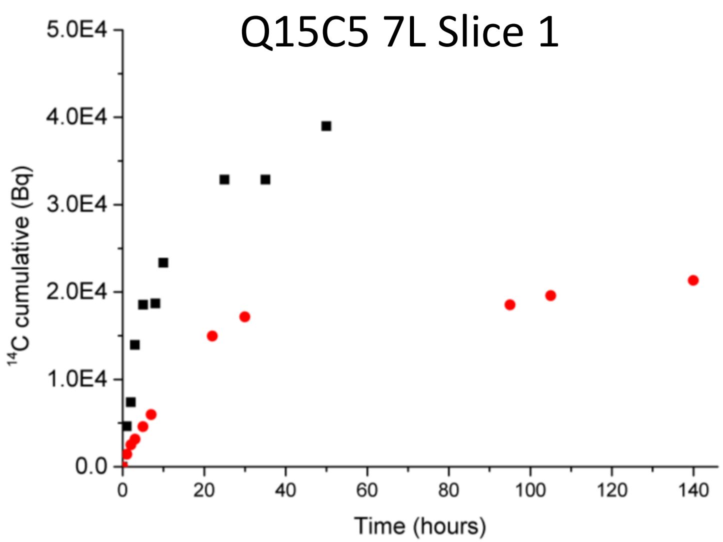
- 600 °C for up to 145 hours (full oxidation)
- 50 mL/min air
- Copper catalyst
- Aliquots taken at 0, 1, 2, 3, 5, 7 hours and others up to final duration (depending on lab access)
- Counted using LSC for 60 minutes

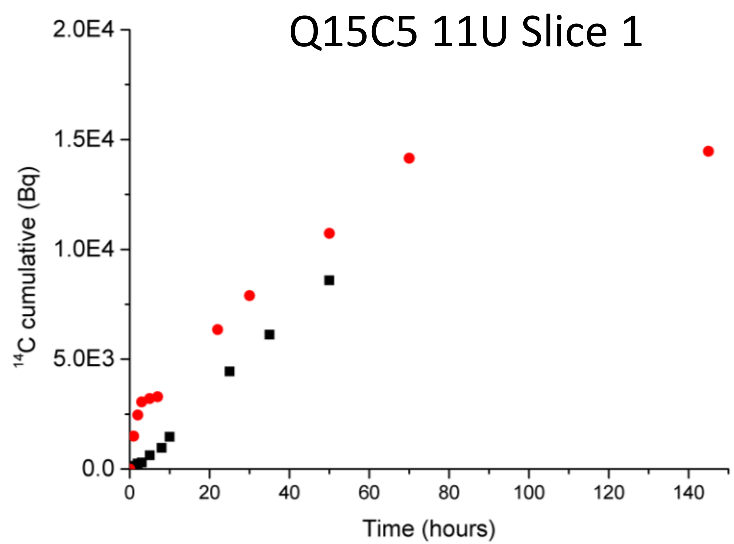
Thermal Oxidation/LSC

Red- 600 °C
Black- 450 °C



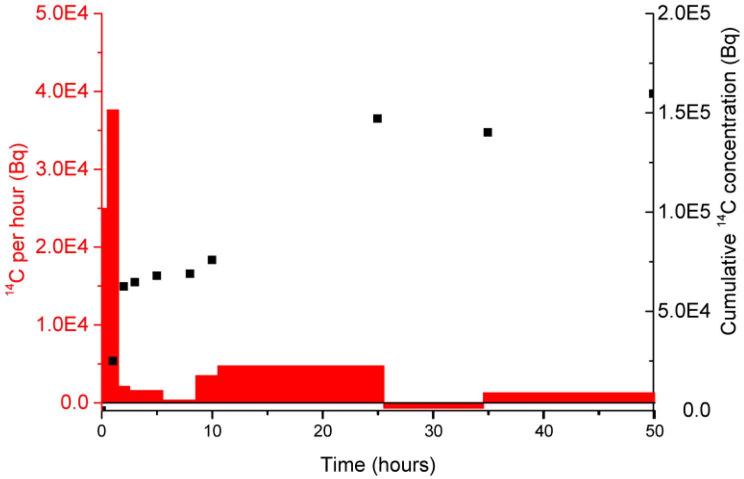




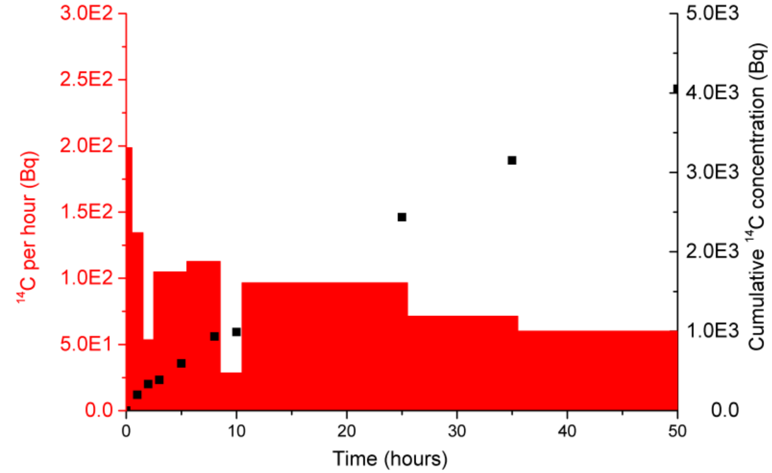


450 °C

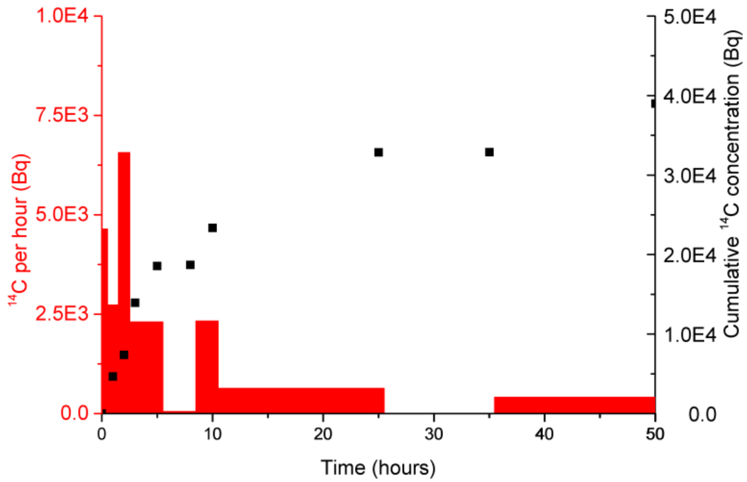
Q15C5 2U Slice 1



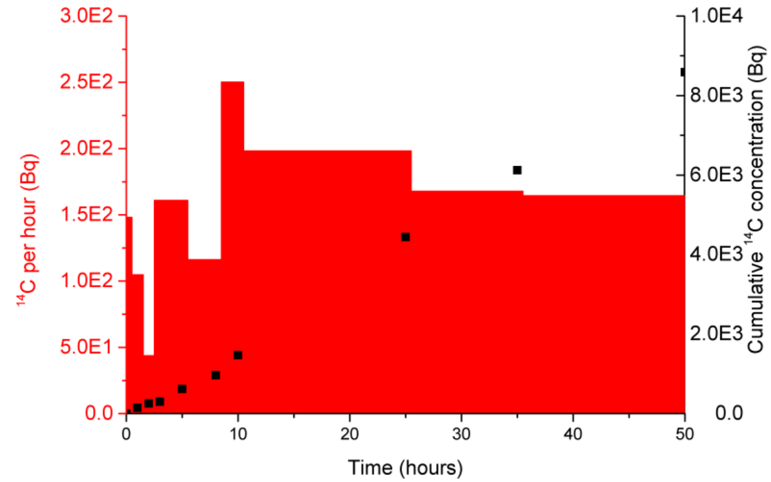
Q15C5 2U Slice 2



Q15C5 7L Slice 1

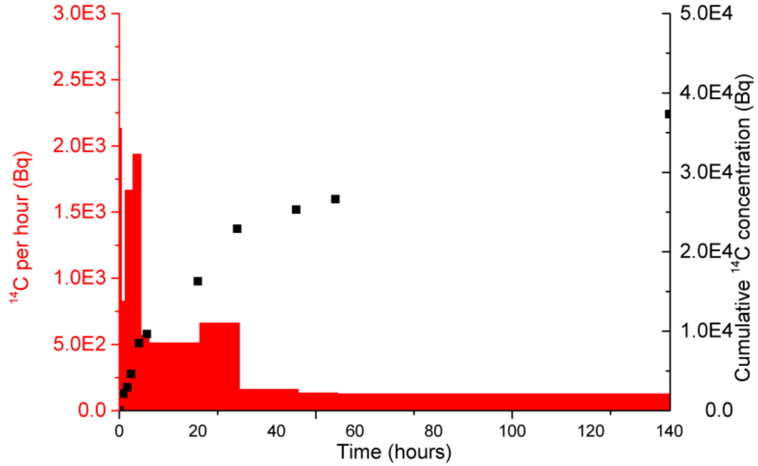


Q15C5 11U Slice 1

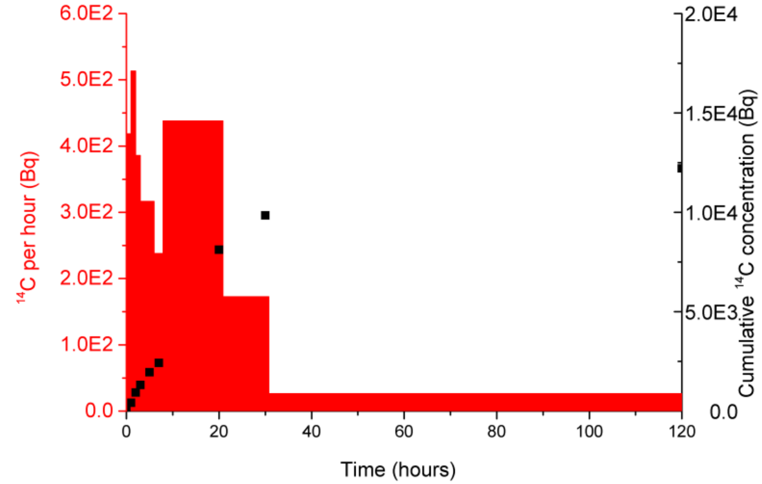


600 °C

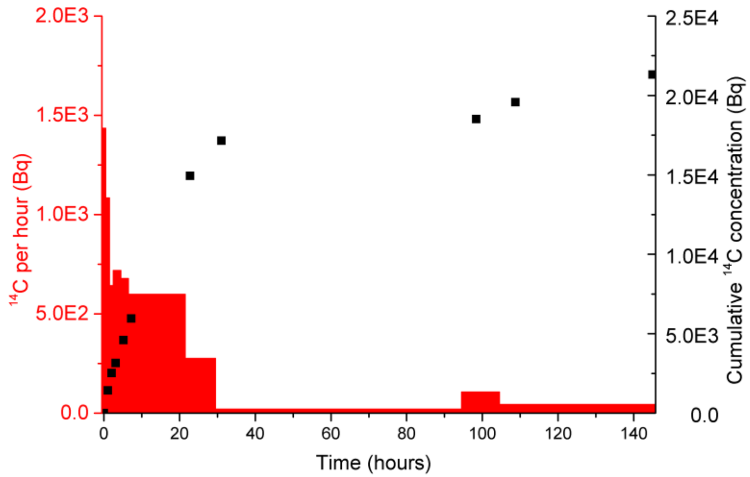
Q15C5 2U Slice 1



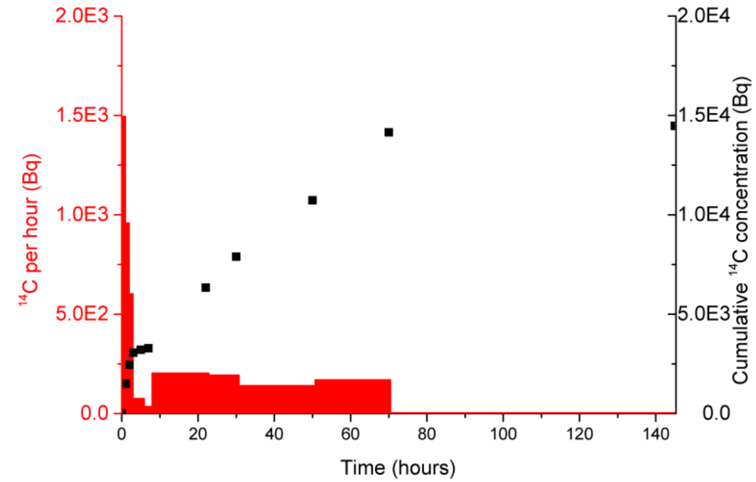
Q15C5 2U Slice 2



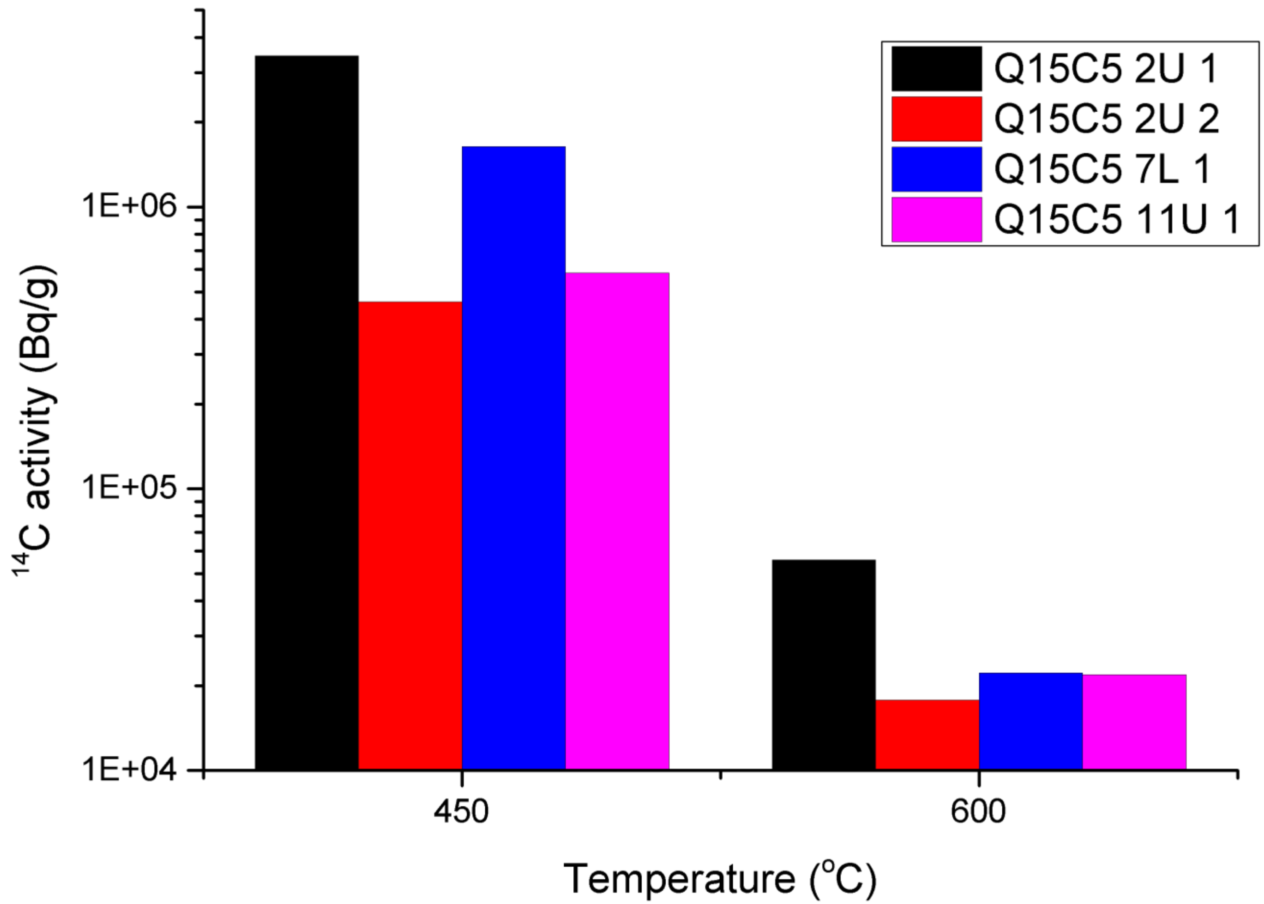
Q15C5 7L Slice 1



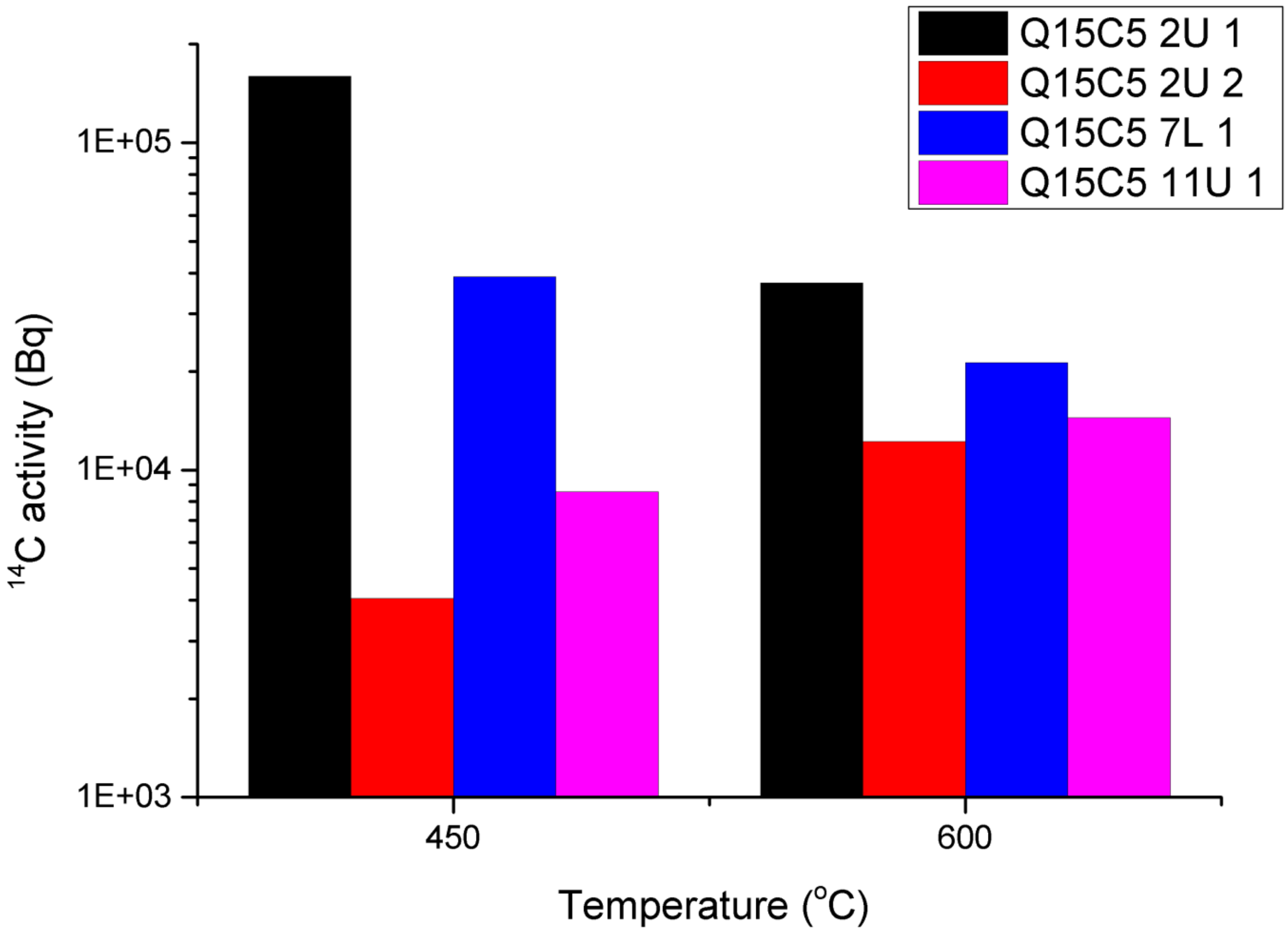
Q15C5 11U Slice 1



Activity per mass



Total activity



Comparison between SIMS/LSC

Mass of ^{14}C (g) =Activity of ^{14}C (Bq)/Specific activity of ^{14}C (1.65×10^{11} Bq/g)

^{14}C concentration (ppm) =Mass of ^{14}C (g)/Mass of material (g)

Sample	**^{14}C concentration SIMS (ppm)**	**^{14}C concentration LSC (ppm)**
Q15C5 2U Slice 1	20.8 ± 3.9	20.9
Q15C5 2U Slice 2	4.1 ± 3.4	2.8
Q15C5 7L Slice 1	13.2 ± 3.9	9.9
Q15C5 11U Slice 1	5.3 ± 1.8	3.5

Thermal Oxidation/LSC Conclusions

- Rapid initial release of ^{14}C at 450 °C from channel wall face samples with significant deposit.
- Inner brick sample still shows significant ^{14}C release at 450 °C
  - Adsorbed precursor species
- Initial release of ^{14}C at 600 °C from all samples
  - Surface (and subsurface) complexes from coolant gas
- Slow later release of ^{14}C at 600 °C from all samples
  - Precursor species located in the graphite lattice

Conclusions

- Samples exposed to channel wall face (usually) have a pronounced carbonaceous deposit present

- Inner brick samples do not have such a deposit but have microstructural changes present associated with a lifetime in a nuclear reactor

- SIMS and LSC analysis highlights a relative enrichment in ^{14}C on the channel wall face deposits.
  - This enrichment appears to be influenced by location within the reactor but not with lifetime neutron dose

- ^{14}C located in this deposit could be more labile than ^{14}C located in bulk graphite

Acknowledgements

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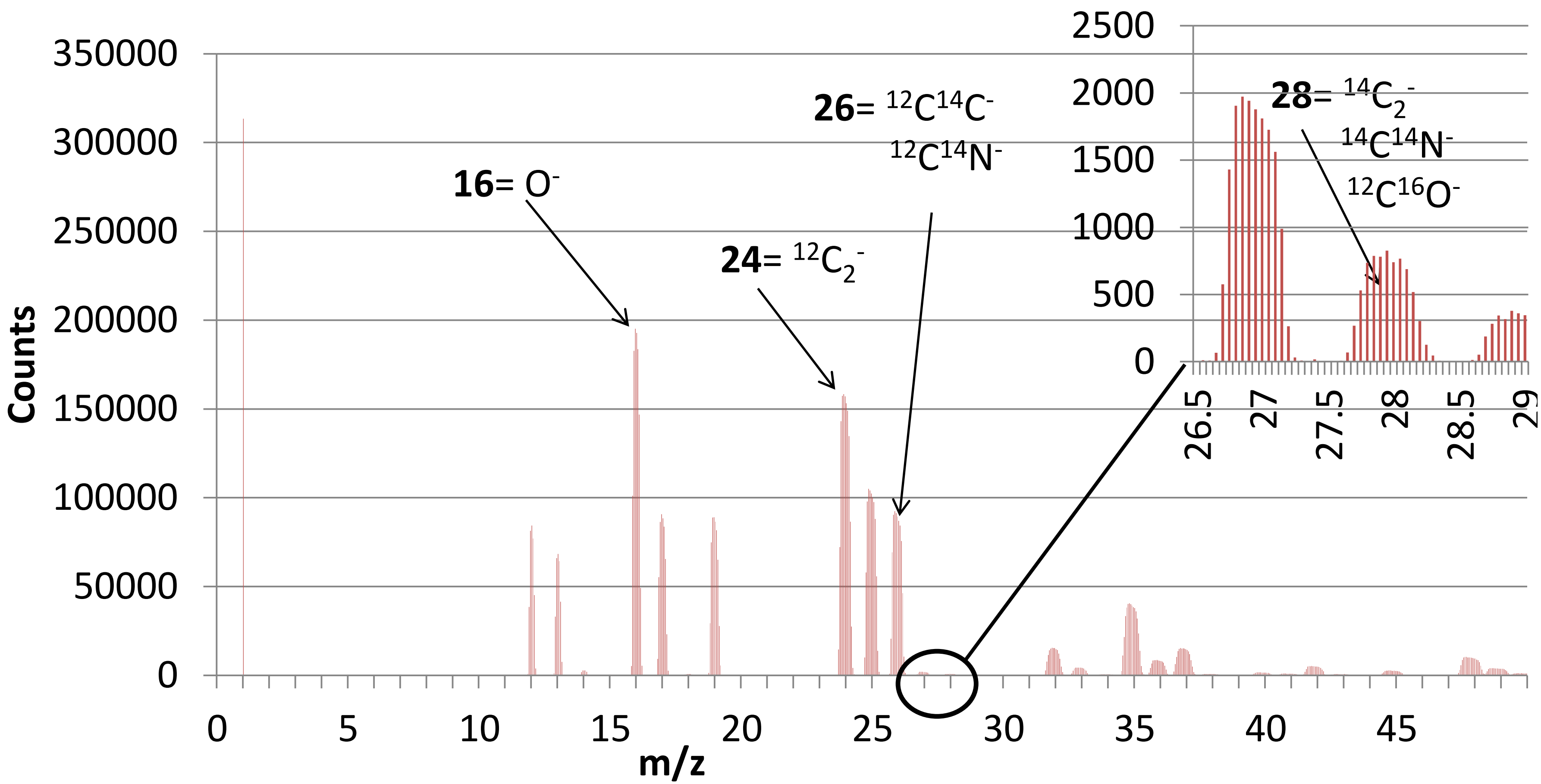
SIMS- Irradiated Graphite



SIMS- Ratios

- **m/z 14:**
  - ^{14}C
  - ^{14}N
  - $^{12}CH_2$
- **m/z 28:**
  - $^{14}C_2$
  - $^{14}C^{14}N$
  - $^{14}C^{12}CH_2$
  - $^{12}C^{16}O$
  - N_2
  - $^{12}CH_2N$
  - Si

More possible ^{14}C containing species

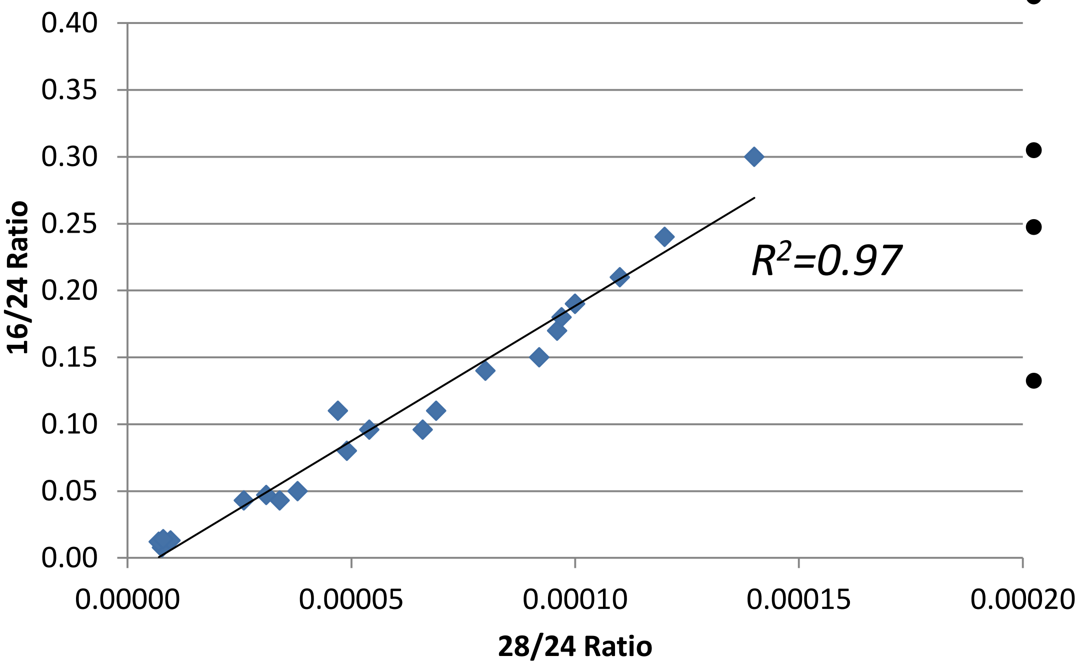
Can investigate effects of oxygen

EDX data suggest these are not present

- Isobaric mass interference effects still present in raw spectra
- Geometrical and location effects on signal
  - use of ratios negates these effects
    - 28:24
    - 16:24

SIMS Experimental

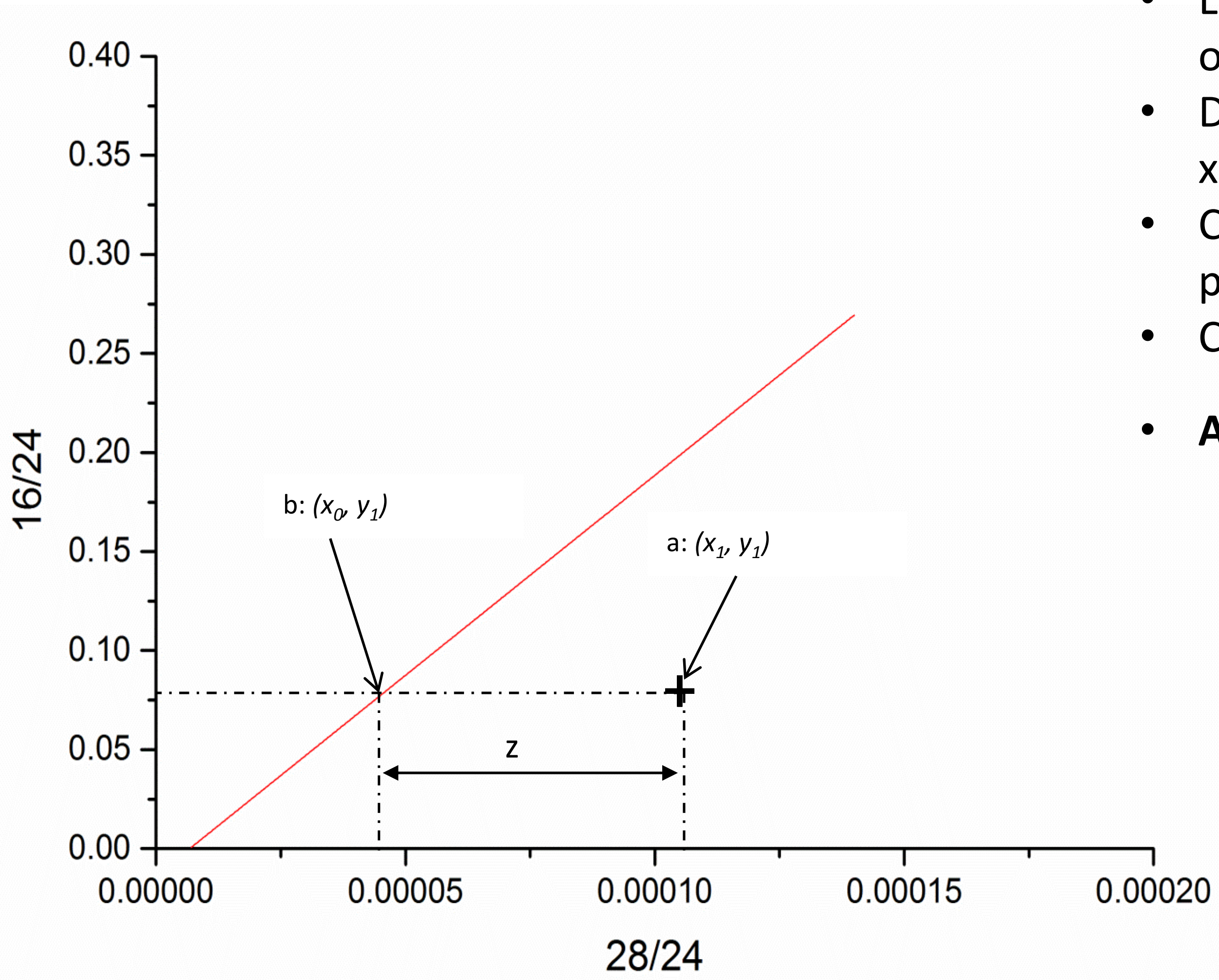
Oxygen Experiment



Irradiated PGA graphite samples

- Depth profile 1800 seconds on 300 μm^2 area
- Depth approximately 300nm
- Six repeats of different areas on each surface
- Ratios calculated
    - 28:24 ($^{14}C_2$: $^{12}C_2$)
    - 16:24 (^{16}O: $^{12}C_2$)
    - 24:(24+26)($^{12}C_2$: $^{12}C_2$ +^{12}CN)

SIMS- Concentration Calculation



- Linear regression performed on oxygen experiment data
- Difference calculated between x_1 and x_0 at point y_1
- Calculated difference in parts per million
- Corrected for CN contribution

- **ASSUMPTIONS**
  - *Signal arising from $^{12}C_2^-$ is constant*
  - *CO species signal generated by injecting oxygen is similar to that found if oxygen is already present*
  - *Corrected signal arising at 28 Da is due to $^{14}C_2^-$*